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**WO 02/051924 A1**

(54) Title: PREPARATION OF DYED PLASTICS OR POLYMERIC DYE PARTICLES

(57) **Abstract:** The present application relates to a process for preparing dyed plastics or polymeric dye particles characterized in that it comprises mixing a high molecular weight organic material with a coloristically effective amount of at least one dye of the formula where R<sub>1</sub> is hydrogen, hydroxyl or a radical -NHCO-R<sub>6</sub>, where R<sub>6</sub> is C<sub>1</sub>-C<sub>6</sub>alkyl or unsubstituted or C<sub>1</sub>-C<sub>4</sub>alkyl- or halogen-substituted phenyl, R<sub>2</sub> is hydrogen, hydroxyl or a radical W-R<sub>7</sub>, where W is -NHCO- or -S- and R<sub>7</sub> is C<sub>1</sub>-C<sub>6</sub>alkyl or unsubstituted or C<sub>1</sub>-C<sub>4</sub>alkyl- or halogen-substituted phenyl, R<sub>3</sub> is hydrogen, R<sub>4</sub> is hydrogen or hydroxyl, R<sub>5</sub> is hydrogen, or R<sub>3</sub> and R<sub>4</sub> combine to form the radical of the formula, where the rings A and B may independently bear further substituents.

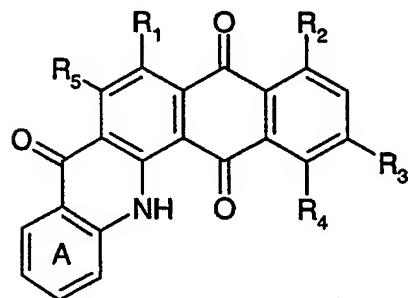
Preparation of dyed plastics or polymeric dye particles

The present invention relates to a process for preparing dyed plastics or polymeric dye particles.

Processes for mass dyeing plastics with dyes are known. However, it has been determined that the dyes hitherto used do not always fully meet the highest requirements, especially with regard to hot light fastness. There is accordingly a need for novel coloration processes which produce light fast and especially hot light fast colorations and exhibit good general fastnesses.

It has now been found that, surprisingly, the coloration process of the invention substantially meets the criteria indicated above.

The present invention accordingly provides a process for preparing dyed plastics or polymeric dye particles, characterized in that it comprises mixing a high molecular weight organic material with a coloristically effective amount of at least one dye of the formula



(1)

where

R<sub>1</sub> is hydrogen, hydroxyl or a radical -NHCO-R<sub>6</sub>, where R<sub>6</sub> is C<sub>1</sub>-C<sub>6</sub>alkyl or unsubstituted or C<sub>1</sub>-C<sub>4</sub>alkyl- or halogen-substituted phenyl,

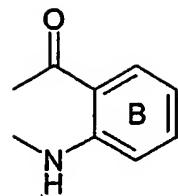
R<sub>2</sub> is hydrogen, hydroxyl or a radical W-R<sub>7</sub>, where W is -NHCO- or -S- and R<sub>7</sub> is C<sub>1</sub>-C<sub>6</sub>alkyl or unsubstituted or C<sub>1</sub>-C<sub>4</sub>alkyl- or halogen-substituted phenyl,

R<sub>3</sub> is hydrogen,

R<sub>4</sub> is hydrogen or hydroxyl,

R<sub>5</sub> is hydrogen, or

$R_3$  and  $R_4$  combine to form the radical of the formula



, where the rings A

and B may independently bear further substituents.

Useful optional substituents for the rings A and B include in particular halogen, C<sub>1</sub>-C<sub>4</sub>alkyl and C<sub>1</sub>-C<sub>4</sub>alkoxy. They may be present more than once.

C<sub>1</sub>-C<sub>6</sub>Alkyls R<sub>6</sub> and R<sub>7</sub> include for example methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, amyl, tert-amyl (1,1-dimethylpropyl), 1,1,3,3-tetramethylbutyl, hexyl, 1-methylpentyl, neopentyl, cyclopentyl, cyclohexyl and the associated isomers.

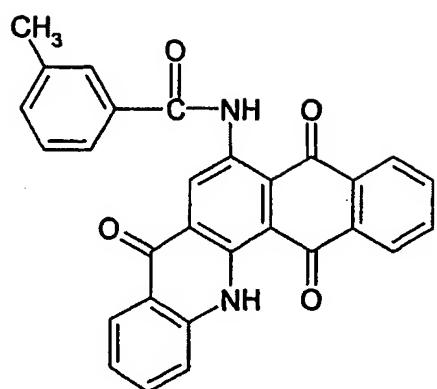
C<sub>1</sub>-C<sub>4</sub>Alkyl as a substituent on phenyl or as a substituent on the rings A and B is methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl and tert-butyl.

C<sub>1</sub>-C<sub>4</sub>Alkoxy as a substituent on the rings A and B is for example methoxy, ethoxy, propoxy and butoxy.

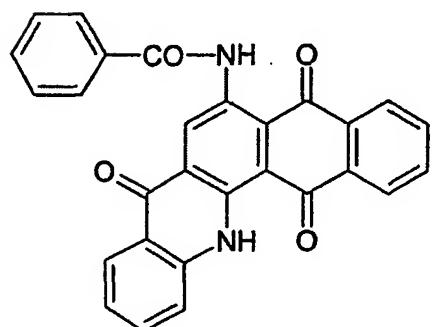
Halogen is bromine, iodine and especially chlorine.

C<sub>1</sub>-C<sub>6</sub>Thioalkyl W-R<sub>7</sub> is for example methylthio, ethylthio, propylthio or butylthio.

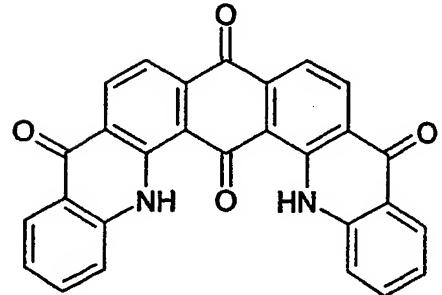
Of the dyes of the formula (1), blue dyes of the formulae



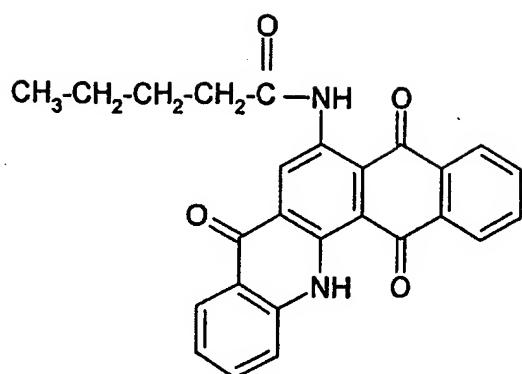
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(3),

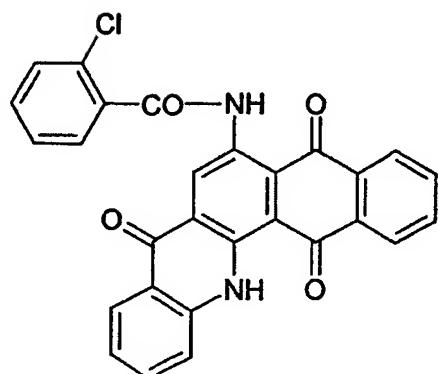


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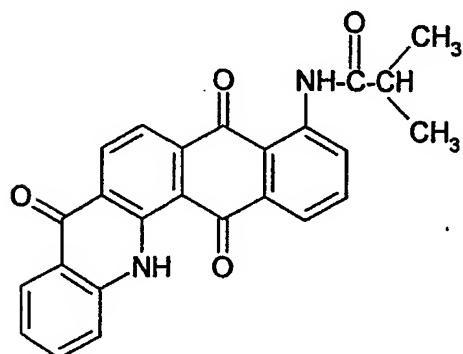
and



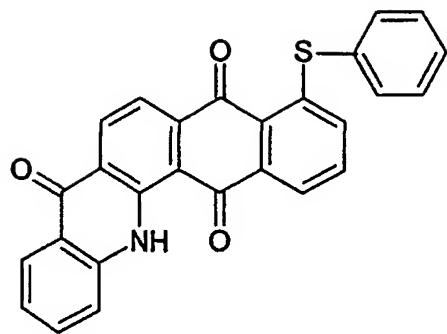
(6)

are preferred.

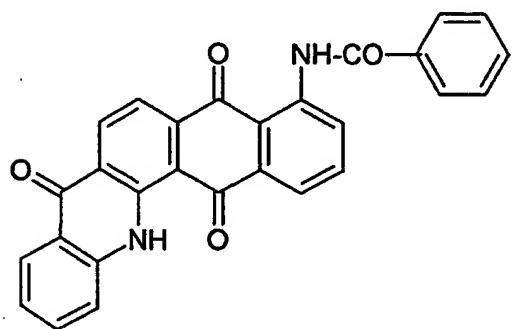
Preference, among the dyes of the formula (1), is likewise given to the red dyes of the formulae



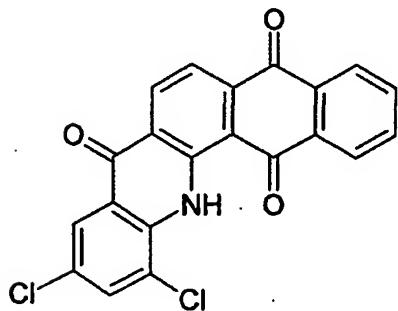
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(8),



(9) and

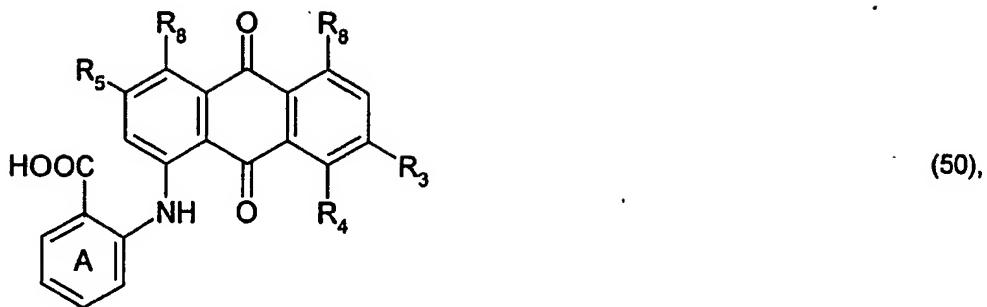


(10).

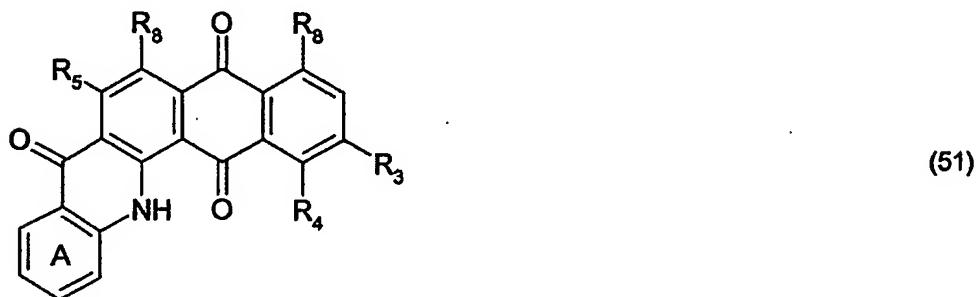
Particular preference is given to the dyes of the formulae (2) and (7).

The dyes used according to the invention are known or preparable similarly to known compounds by generally known methods.

The dyes of the formula (1) which are used according to the invention are prepared for example by ring closure of compound of a formula



where A, R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> are each as defined under the formula (1) and one of the R<sub>8</sub> substituents is -NH<sub>2</sub> and the other is R<sub>1</sub> or R<sub>2</sub>, in chlorosulfonic acid to form the compound of the formula



and subsequent reaction thereof with a carbonyl chloride to form the dye of the formula (1).

The compounds of the formula (50) are known or are preparable similarly to known compounds by generally known methods.

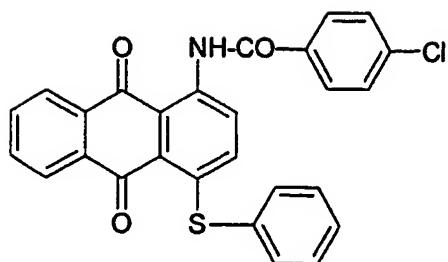
The high molecular weight organic substances are dyed with the dye of the formula (1) for example by mixing said dye into these substrates using roll mills or mixing or grinding apparatus whereby the dye is dissolved or finely dispersed in the high molecular weight material. The high molecular weight organic material with the admixed dye is then processed in a conventional manner, for example by calendering, pressing, extrusion, spread coating, spinning, casting or injection moulding, whereby the dyed material acquires its ultimate shape. The admixing of the dye can also be effected directly prior to the actual processing step, for example by continuously metering a solid, for example pulverulent, dye and a granulated or pulverulent high molecular weight organic material and also optionally additional substances such as for example additives simultaneously directly into the inlet zone of an extruder where the mixing-in takes place just prior to the processing. In general,

however, prior mixing of the dye into the high molecular weight organic material is preferable, since more uniformly dyed substrates are obtainable.

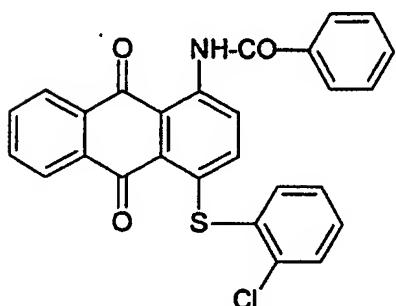
It is often desired to incorporate plasticizers into the high molecular weight compounds prior to shaping to produce non-rigid mouldings or to reduce their brittleness. Useful plasticizers include for example esters of phosphoric acid, phthalic acid or sebacic acid. In the process of the present invention, plasticizers can be incorporated into the polymers before or after colorant has been incorporated. It is further possible, for the purpose of achieving different hues, to add to the high molecular weight organic substances not only the dye of the formula (1) but also further pigments or other colorants in any desired quantities, optionally together with further additives, for example fillers or siccatives.

Preference is given to colouring thermoplastics especially in the form of fibres. Preferred high molecular weight organic materials which are colourable according to the invention are in general polymers having a dielectric constant  $\geq 2.5$ , especially polyester, polycarbonate (PC), polystyrene (PS), polymethyl methacrylate (PMMA), polyamide, polyethylene, polypropylene, styrene/acrylonitrile (SAN) or acrylonitrile/butadiene/styrene (ABS). Particular preference is given to polyester and polyamide. Very particular preference is given to linear aromatic polyesters obtainable by polycondensation of terephthalic acid and glycols, especially ethylene glycol, or condensation products of terephthalic acid and 1,4-bis(hydroxymethyl)cyclohexane, for example polyethylene terephthalate (PET) or polybutylene terephthalate (PBTP); polycarbonates, for example polycarbonates formed from  $\alpha,\alpha$ -dimethyl-4,4'-dihydroxydiphenylmethane and phosgene; or polymers based on polyvinyl chloride or polyamide, for example nylon 6 or nylon 66.

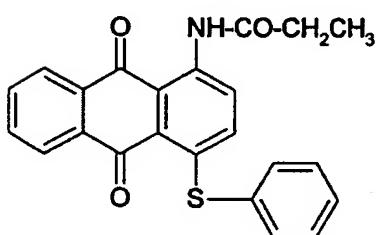
The present invention further provides a process for trichromatic dyeing of plastics or polymeric dye particles which is characterized in that it comprises mixing at least one blue-dyeing dye of the formulae (2), (3), (4), (5) or (6), at least one red-dyeing dye of the formulae (7), (8), (9), (10),



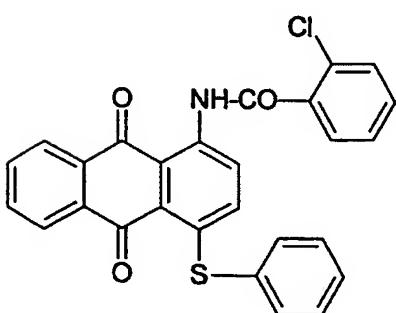
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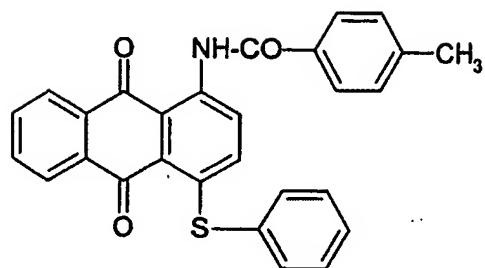
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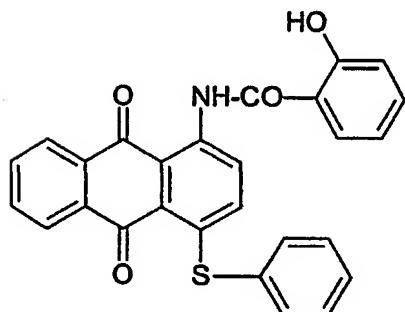
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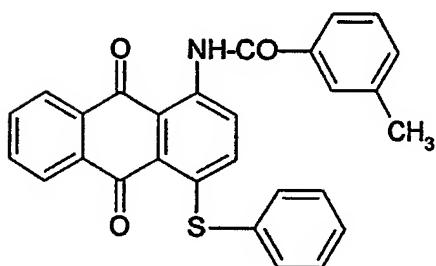
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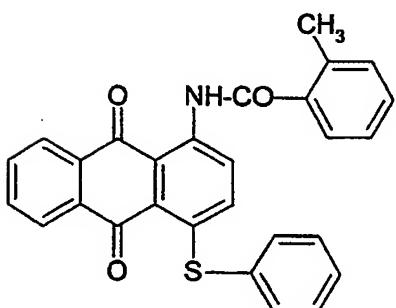
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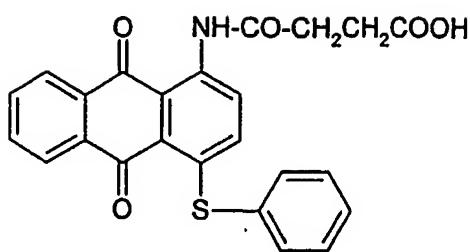
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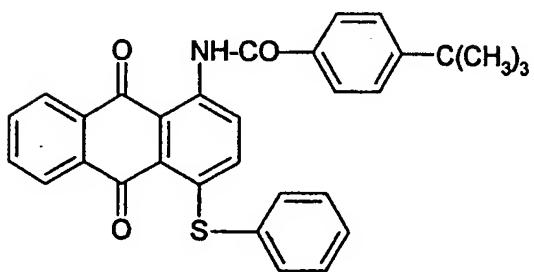
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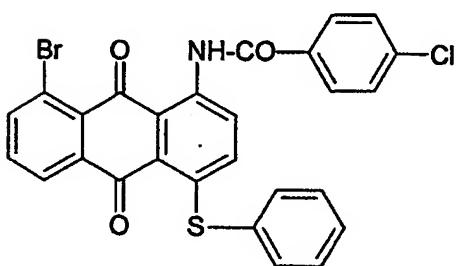
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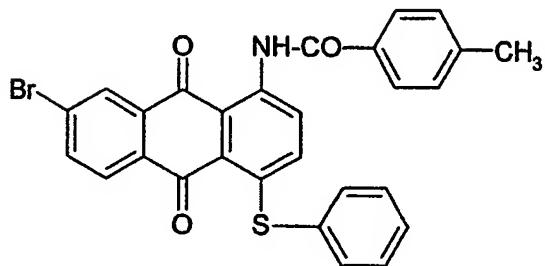
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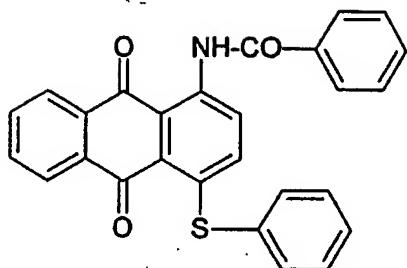
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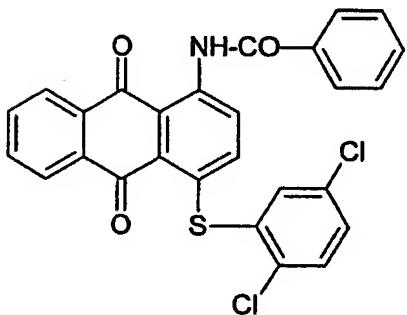
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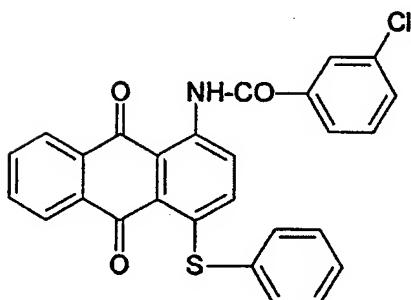
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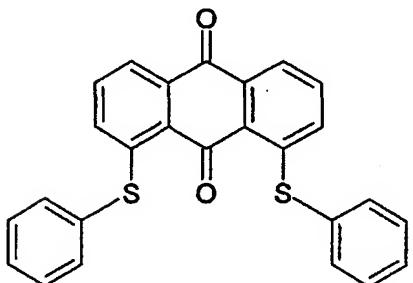


(24) or



(25)

and the yellow-dyeing dye of the formula



(26)

into the plastics or polymeric dye particles.

The dyes of the formula (11) to (26) are known or preparable similarly to known compounds by processes known per se.

Trichromism is the additive colour mixture of appropriately selected yellow- or orange-, red- and blue-dyeing dyes whereby any desired hue of the visible spectrum can be matched by suitable choice of the amount ratios of the dye components.

A preferred embodiment of the trichromatic process according to the invention is characterized in that the blue-dyeing dye of the formula (2) is used together with the red-dyeing dye of the formula (7) and the yellow-dyeing dye of the formula (26).

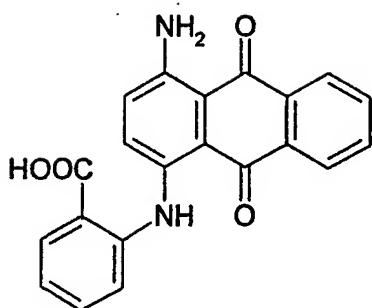
A further preferred embodiment of the trichromatic process according to the invention is characterized in that the blue-dyeing dye of the formula (2) is used together with the red-dyeing dye of the formula (14) and the yellow-dyeing dye of the formula (26).

The dyes used according to the invention confer on the aforementioned materials, especially the polyester and polyamide materials, strong level hues having good user fastnesses, especially very good light fastness.

The examples hereinbelow illustrate the invention. Parts and percentages are by weight, unless otherwise stated. Temperatures are in degrees Celsius. Parts by weight relate to parts by volume as the gram relates to the cubic centimetre.

Example 1:

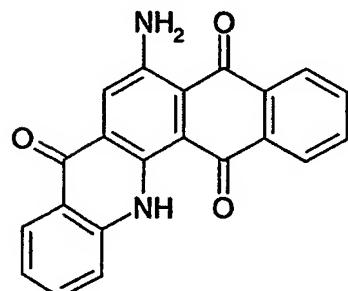
A reaction vessel is charged with 145.0 parts by weight of concentrated sulfuric acid and 70.0 parts by weight of chlorosulfonic acid. 36.0 parts by weight of the compound of the formula



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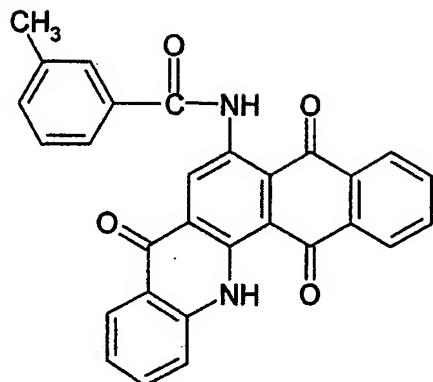
are added at 25°C and the mixture is subsequently stirred at 25-30°C for 2 hours. It is then discharged onto 1 500 parts by weight of ice water and the precipitated product is filtered off with suction, washed neutral and dried.

This provides 32.0 parts by weight of the compound of the formula



(53).

12.9 parts by weight of the compound of the formula (53) are introduced into 85 parts by weight of nitrobenzene and the mixture is heated to 130-140°C. A solution of 6.6 parts by weight of m-tolyl chloride in 12 parts by weight of nitrobenzene is added dropwise over about 30 minutes at 130-140°C. The mixture is subsequently stirred for 1 hour. The reaction mixture is then cooled down to 20-40°C, filtered directly or after dilution with methanol, and the filter residue is washed with methanol and water and dried. This provides 14.8 parts by weight of the dye of the formula

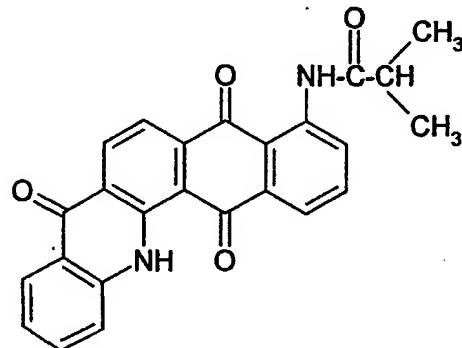


(2),

which dyes polyester in a lightfast blue shade.

Example 2:

1 200.00 g of polyester chips (PET Arnite D04-300, DSM) are predried at 130°C for 4 hours and subsequently mixed with 0.24 g of the dye of the formula



(7),

in a roller rack at 60 revolutions per minute for 15 minutes until homogeneous.

The homogeneous mixture is extruded on a twin screw 25 mm extruder from Collin, D-85560 Ebersberg comprising 6 heating zones at a maximum temperature of 275°C, quenched with water; pelletized in a Turb Etuve TE 25 pelletizer from MAPAG AG, CH-3001 Bern and subsequently dried at 75°C for 4 hours.

This provides red polyester chips having good all-round fastnesses, especially very good light and hot light fastnesses.

Example 3:

1 200.00 g of polyester chips (PET Arnite D04-300, DSM) are predried at 130°C for 4 hours and subsequently mixed with

0.64 g of the dye of the formula (2),

0.30 g of the dye of the formula (7) and

1.46 g of the dye of the formula (26)

in a roller rack at 60 revolutions per minute for 15 minutes until homogeneous.

The homogeneous mixture is extruded on a twin screw 25 mm extruder from Collin, D-85560 Ebersberg comprising 6 heating zones at a maximum temperature of 220°C, quenched with water, pelletized in a Turb Etuve TE 25 pelletizer from MAPAG AG, CH-3001 Bern and subsequently dried at 75°C for 4 hours.

This provides grey polyester chips having good all-round fastnesses, especially very good light and hot light fastnesses.

Example 4:

1 200.00 g of polyester chips (PET Arnite D04-300, DSM) are predried at 130°C for 4 hours and subsequently mixed with

2.40 g of the dye of the formula (2)

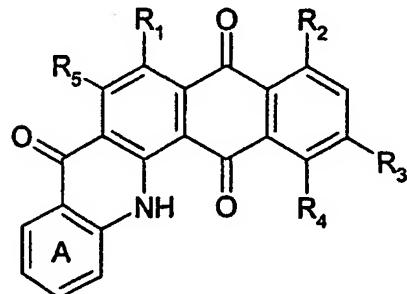
in a roller rack at 60 revolutions per minute for 15 minutes until homogeneous.

The homogeneous mixture is extruded on a twin screw 25 mm extruder (from Collin, D 85560 Ebersberg) comprising 6 heating zones at a maximum temperature of 220°C, quenched with water, granulated in a Turb Etuve TE 25 granulator (from MAPAG AG, CH 3001 Bern) and subsequently dried at 75°C for 4 hours.

This provides blue polyester chips having good all-round fastnesses, especially very good light and hot light fastnesses.

WHAT IS CLAIMED IS:

1. A process for preparing dyed plastics or polymeric dye particles characterized in that it comprises mixing a high molecular weight organic material with a coloristically effective amount of at least one dye of the formula



(1)

where

R<sub>1</sub> is hydrogen, hydroxyl or a radical -NHCO-R<sub>6</sub>, where R<sub>6</sub> is C<sub>1</sub>-C<sub>6</sub>alkyl or unsubstituted or C<sub>1</sub>-C<sub>4</sub>alkyl- or halogen-substituted phenyl,

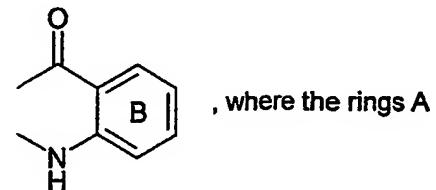
R<sub>2</sub> is hydrogen, hydroxyl or a radical W-R<sub>7</sub>, where W is -NHCO- or -S- and R<sub>7</sub> is C<sub>1</sub>-C<sub>6</sub>alkyl or unsubstituted or C<sub>1</sub>-C<sub>4</sub>alkyl- or halogen-substituted phenyl,

R<sub>3</sub> is hydrogen,

R<sub>4</sub> is hydrogen or hydroxyl,

R<sub>5</sub> is hydrogen, or

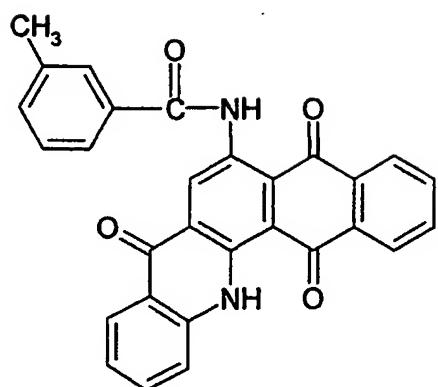
R<sub>3</sub> and R<sub>4</sub> combine to form the radical of the formula



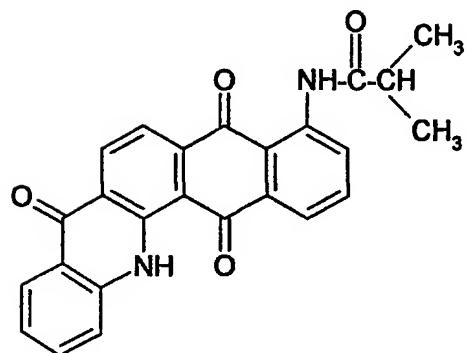
, where the rings A

and B may independently bear further substituents.

2. A process according to claim 1, characterized in that dyes of the formulae



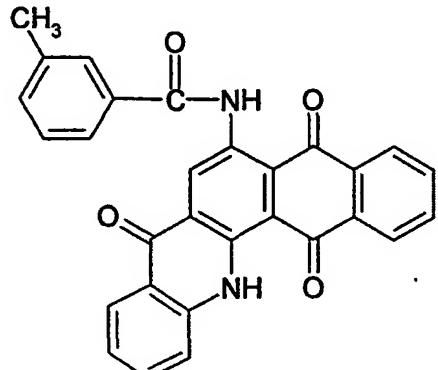
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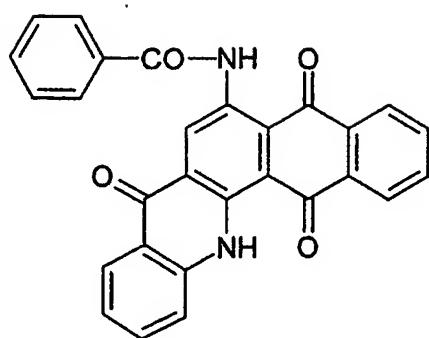
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are used.

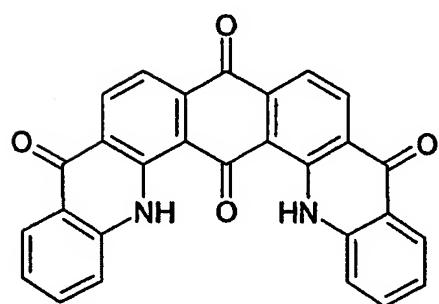
3. A process for trichromatic dyeing of plastics or polymeric dye particles characterized in that it comprises mixing at least one blue-dyeing dye of the formulae



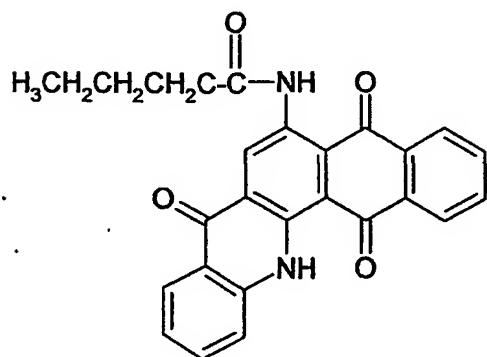
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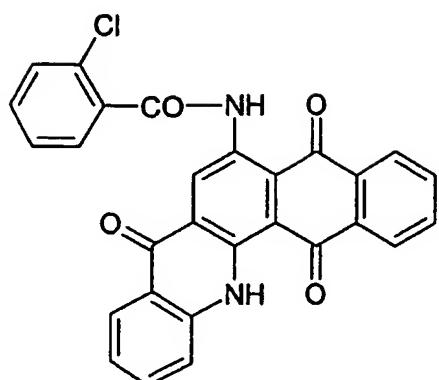
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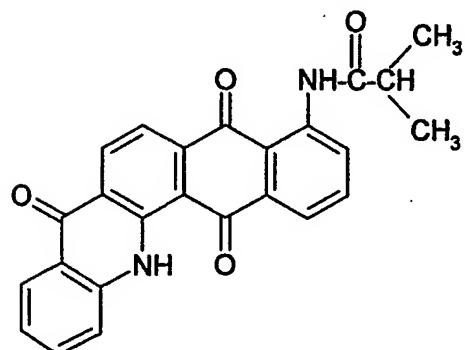


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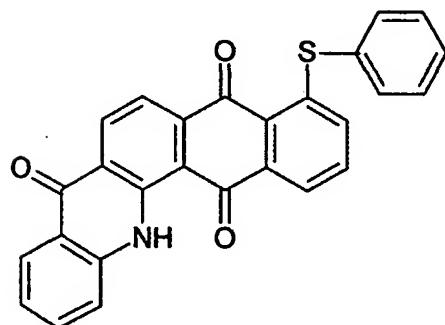


(6),

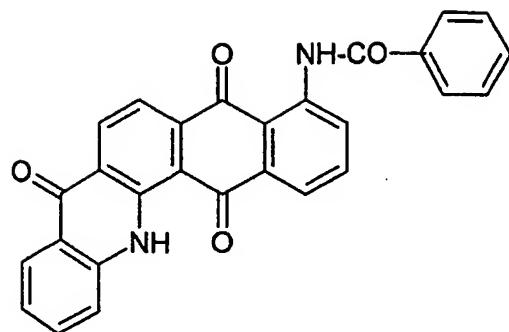
at least one red-dyeing dye of the formulae



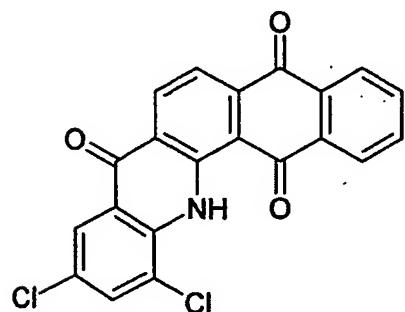
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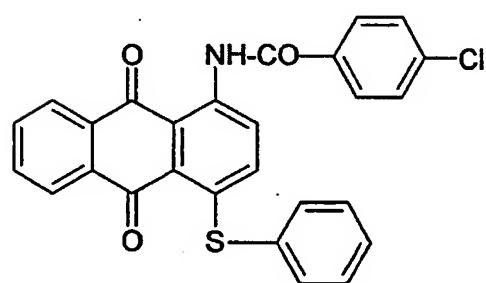
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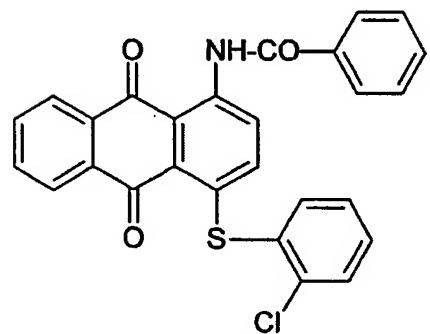
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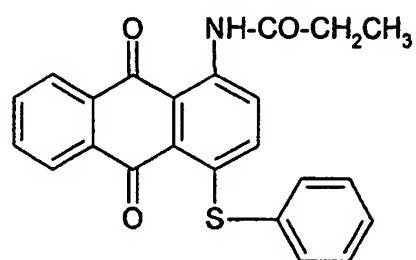
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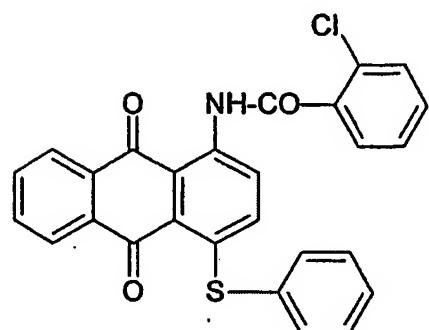
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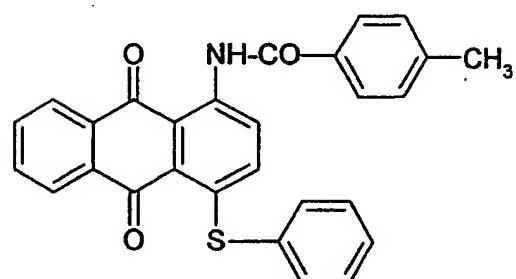
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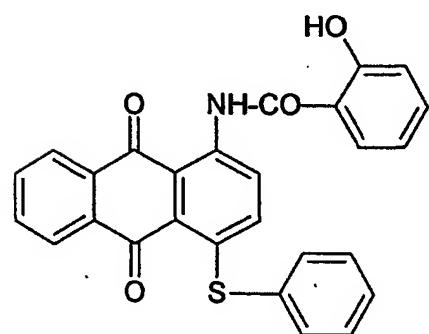
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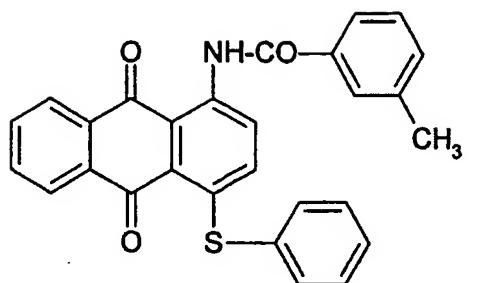
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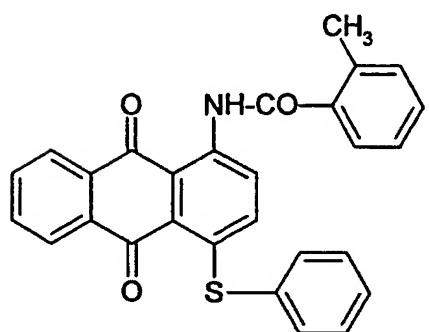
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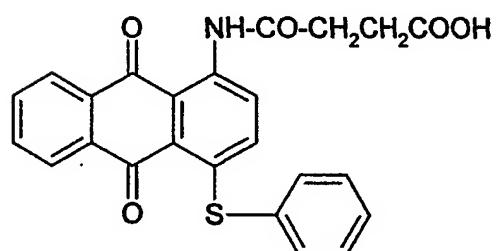
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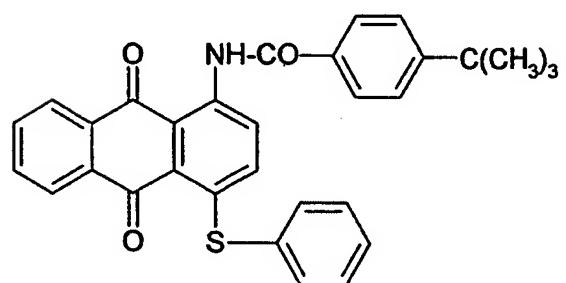
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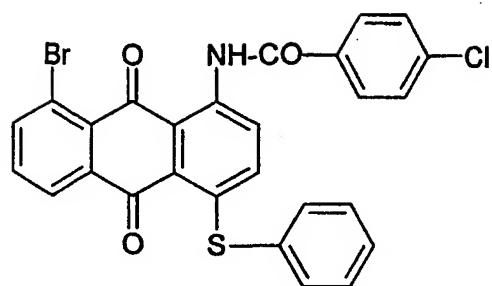
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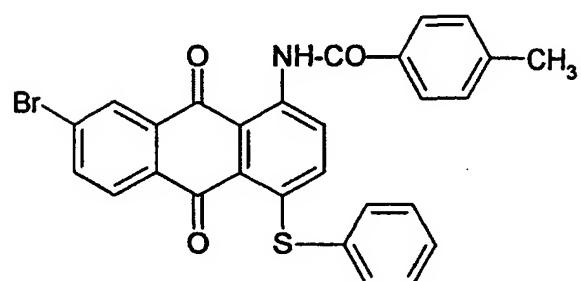
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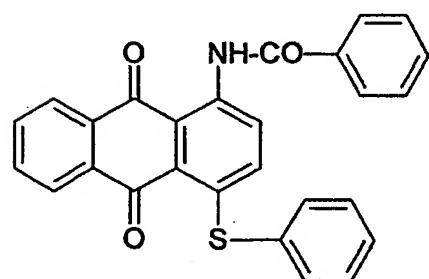
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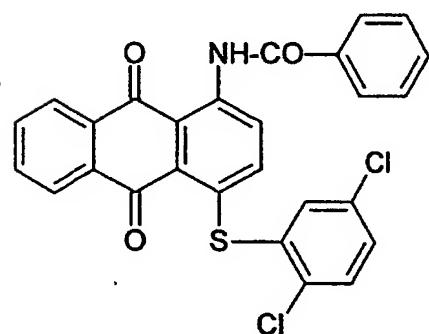
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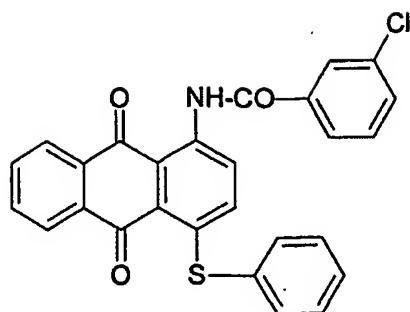
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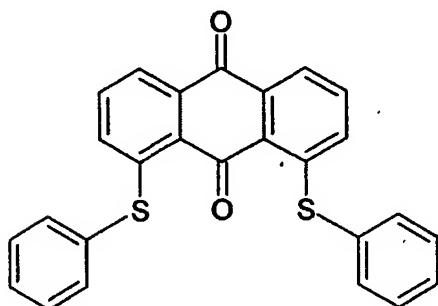


(24) or



(25),

and the yellow-dyeing dye of the formula



(26)

into the plastics or polymeric dye particles.

4. The dyed plastic or polymeric dye particles prepared by the process of either of claims 1 and 2.

5. The use of dyes of the formula (1) according to claim 1 for preparing dyed plastics or polymeric dye particles.

## INTERNATIONAL SEARCH REPORT

Ir — onal Application No  
PCT/EP 01/14691A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08K5/3437 C09B5/34

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08K C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 022 652 A (BASF AG) 16 March 1966 (1966-03-16) the whole document	1,4,5
X	FR 2 192 142 A (CIBA GEIGY AG) 8 February 1974 (1974-02-08) the whole document	1,4,5

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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- "O" document referring to an oral disclosure, use, exhibition or other means
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- "&" document member of the same patent family

Date of the actual completion of the International search

22 April 2002

Date of mailing of the international search report

29/04/2002

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Authorized officer

Ginoux, C

## INTERNATIONAL SEARCH REPORT

Information on patent family members

In tional Application No

PCT/EP 01/14691

Patent document cited in search report	Publication date		Patent family member(s)	Publication date
GB 1022652	A 16-03-1966	DE BE CH FR	1180933 B 627049 A 422325 A 1345379 A	05-11-1964 15-10-1966 06-12-1963
FR 2192142	A 08-02-1974	CH AR AU AU BE DE FR GB IT JP NL	570436 A5 198673 A1 469808 B 5721673 A 802017 A1 2334064 A1 2192142 A1 1385003 A 991031 B 49058146 A 7309349 A	15-12-1975 15-07-1974 26-02-1976 09-01-1975 07-01-1974 24-01-1974 08-02-1974 26-02-1975 30-07-1975 05-06-1974 09-01-1974

Form PCT/ISA/210 (patent family annex) (July 1992)